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## PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

## Production of Aromatic Carboxylic Acids or Derivatives Thereof

We, HALCON INTERNATIONAL INC., of 2, Park Avenue, New York 16, New York, United States of America, a corporation organized and existing under the laws of the State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention is concerned with the production of aromatic carboxylic acids or derivatives thereof from aromatic compounds.

Aromatic acids and compounds which are easily converted to aromatic acids have very great commercial significance. Aromatic diacids as terephthalic acid are consumed in very great amounts in the preparation of polyesters, for example. Although methods are presently known for the production of aromatic acids the present methods involve the use of relatively costly raw materials and/or the use of rather elaborate processing sequences. The art has actively sought improved methods for the production of aromatic acids or derivatives thereof which can be readily converted to the aromatic acids.

It has now been found that aromatic hydrocarbons can be subjected to an oxy-carbonylation reaction with the direct production of aromatic carboxylic acids or derivatives thereof.

According to the present invention, an aromatic carboxylic acid or a derivative thereof is produced by the reaction of an aromatic compound, carbon monoxide and a metal salt oxidant.

The process of the invention is generally applicable to aromatic compounds. Suitable aromatic compounds which may be reacted in accordance therewith are benzene, naphthalene, or a substituted benzene or naph-

thalene. Examples of substituent groups which may be present on the benzene or naphthalene nucleus are alkyl groups, aryl groups, and hydroxy, alkoxy, amido, halo, acyloxy and aryloxy groups. Thus examples of aromatic compounds which may be reacted in the process of this invention are benzene, toluene, the xylenes, ethylbenzene, isopropyl benzene, diphenyl, phenol, phenyl acetate, resorcinol, methyl phenyl ether, acetanilide, chlorobenzene and diphenyl ether.

The oxidant metal salts are preferably salts of ruthenium, rhodium, palladium, osmium, iridium and platinum. The oxidants are employed in the form of salts, with the chloride being preferred although other salts including the acetate, sulphate, nitrate, phosphate, borate, bromide, fluoride, iodide and silicate are also suitable. By far the outstanding and preferred species of metal oxidant is palladium chloride.

The reaction is carried out either in the liquid or the vapour phase. The aromatic hydrocarbon is contacted with the carbon monoxide and the oxidant salt at reaction conditions. Temperatures generally are in the range of 25° to 250°C and preferably 50° to 150°C. Pressures generally ranging from atmospheric to 3000 p.s.i.g. can be employed with a preferred pressure range being 50 to 1000 p.s.i.g.

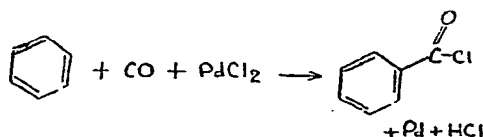
Where the reaction is carried out in the liquid phase, a solvent which is non-reactive in the system can be employed. Illustrative non-reactive solvents are acetone, nitrobenzene and acetic acid.

The metal oxidant salt is partially or completely reduced during the course of the reaction. The reduced metal can be reoxidized for re-use in the process by oxidation with, for example, chlorine, nitric acid or oxygen.

It is advantageous, regardless of the nature of the oxidant salt, to carry out the oxycar-

bonylation in the presence of added hydrogen chloride. This is true for either the liquid or vapour phase embodiments. It is generally not desirable to have present significant quantities of water or reactive alcohols, that is aliphatic primary or secondary alcohols although minor amounts of these materials can be present.

The reaction of the invention is illustrated, by way of example, by the following equation which shows the conversion of benzene to the acid chloride derivative:



With substituted aromatics, the product comprises a mixture of the various isomers. When metal salts other than the chloride are employed, the product will vary corresponding to the anion of the metal salt. Where the reaction is carried out in the presence of water or reactive alcohol, the aromatic product of the reaction will further react with the water of alcohol to form the corresponding acid or ester directly.

Catalysts may be employed along with the metal salt oxidants cited above. Catalysts can improve the rate of the oxycarbonylation reaction. They also serve to promote the reoxidation of the recovered, reduced metal oxidant and are most easily recycled with the metal oxidant. The catalysts are multivalent metals such as Cu, Fe, Mn, Co, and are preferably employed as salts, most preferably as chlorides. The catalysts are employed in amounts of 0.01 to 10 moles per mole of metal oxidant preferably in amounts of 0.1 to 2 moles per mole of oxidant.

The metal salt oxidants can be employed in molar or greater amounts as well as in considerably less than molar amounts. In the latter case, the oxidant can be regenerated from the reduced form by in situ oxidation. The oxidants can be employed as soluble salts in liquid phase reaction or as solids dispersed in the liquid phase. In vapour phase reactions, the metal salts are preferably supported on a solid support, e.g., alumina.

By the term "aromatic acid" as used herein is meant a compound having the acid group attached to an aromatic ring carbon.

#### EXAMPLE 1

A mixture of 9.0 grams of  $\text{PdCl}_2$  and 80 grams of toluene is charged to an electrically heated 150 cc steel vessel. The charge is heated to  $150^\circ$  and pressured to 670 p.s.i.g. with carbon monoxide. After five hours the pressure has dropped to 530 p.s.i.g. and the

reaction is stopped. The effluent is treated with water to hydrolyze acid chlorides and analyzed. A yield of 31.5% toluic acids based on  $\text{PdCl}_2$  is obtained. The toluic acids consists of approximately equal amounts of ortho, meta and para isomers.

#### EXAMPLE 2

Example 1 is duplicated except that benzene is substituted for toluene. A 25% yield of benzoyl chloride based on  $\text{PdCl}_2$  is obtained.

#### EXAMPLE 3

A solid catalyst is prepared by immersing 100 grams of 1/16" eta alumina extrudates in a solution prepared from 7.5 grams  $\text{CuCl}_2$ , 2.5 grams  $\text{PdCl}_2$ , 15 ml. concentrated hydrochloric acid (37%) and 15 mol water. The excess liquid is removed by filtration and the catalyst dried.

A gaseous mixture of benzene, carbon monoxide, oxygen and hydrogen chloride in the mole ration of 2:2:1:2 is passed over the catalyst in a reaction tube. The temperature is  $225^\circ\text{C}$ , the pressure 200 p.s.i.g. and the space velocity 200  $\text{hr}^{-1}$ . Analysis of the effluent indicates the presence therein of substantial amounts of benzoyl chloride product.

In Patent Specification No. 1065343, there is claimed a process for the substitution of carboxylic acid halide groups for nuclear hydrogen atoms in aromatic compounds having carboxylic rings or such compounds when substituted but having at least one unsubstituted hydrogen atom on the aromatic ring, by reacting such a compound with a halocarbon or halo hydrocarbon and carbon monoxide in the presence of a catalyst comprising a metal which is capable of forming a carbonyl or carbonyl halide compound, or a compound of such a metal.

In the process of the present invention for the production of an aromatic carboxylic acid or a derivative thereof no halocarbon or halo hydrocarbon is added as a reactant.

#### WHAT WE CLAIM IS:

1. A process for the production of an aromatic carboxylic acid or a derivative thereof which comprises reacting an aromatic compound with carbon monoxide and a metal salt oxidant in the absence of added halocarbon or halo hydrocarbon.

2. A process according to claim 1 in which the metal salt oxidant is selected from salts of ruthenium, rhodium, palladium, osmium, iridium and platinum.

3. A process according to claim 1 or 2 in which the reaction is carried out in the presence of hydrogen chloride.

4. A process according to any one of the preceding claims, in which the metal salt is palladium chloride.

5. A process according to any one of the preceding claims, in which the reaction is carried out in the liquid phase.
6. A process according to any of claims 1 to 4, in which the reaction is carried out in the vapour phase.
7. A process according to any one of the preceding claims, in which the aromatic compound is toluene, xylene or benzene.
- 10 8. A process according to any one of the preceding claims, in which the reaction is carried out at a temperature of from 25° to 250°C. and under a pressure from atmospheric pressure to 3000 p.s.i.g.
- 15 9. A process according to claim 8, in which the temperature is from 50° to 150°C. and the pressure is from 50 to 1000 p.s.i.g.
- 20 10. A process as claimed in any one of the preceding claims, in which the reaction is carried out in the presence of a multi-valent metal catalyst.
11. A process as claimed in claim 10, in which the metal catalyst is a copper, iron, manganese or cobalt catalyst.
12. A process as claimed in any one of the preceding claims in which the reduced metal salt oxidant is regenerated and re-used in the process. 25
13. A process as claimed in claim 1, substantially as hereinbefore described and exemplified. 30
14. An aromatic carboxylic acid or a derivative thereof, when produced by the process of any one of the preceding claims.

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